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(21) International Application Number: PCT/EP93/02486 (22) International Filing Date: 14 September 1993 (14.09.93) (30) Priority data: 3012/92-0 25 September 1992 (25.09.92) CH (71) Applicant (for all designated States except US): CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH). (72) Inventors; and (75) Inventors/Applicants (for US only) : HOFFMANN, Kurt [DE/DE]; Heidenbergstrasse 15, D-64686 Lautertal 2 (DE). HERBST, Heinz [DE/DE]; Hohensteiner Strasse 40, D-64686 Lautertal-Reichenbach (DE). PFAENDER, Rudolf [DE/DE]; Sackgasse 3, D-64668 Rimbach am Odenwald 1 (DE). SANDER, Hans, Jürgen [DE/DE]; Magnolienstrasse 25, D-64653 Lorsch (DE). SI-TEK, Franciszek [CH/CH]; Grossmattweg 11, CH-4106 Therwil (CH).		(74) Common Representative: CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS FOR THE STABILIZATION OF AND STABILIZER MIXTURES FOR RECYCLED PLASTICS (57) Abstract Recycled plastics, predominantly thermoplastics, from domestic, commercial and industrial waste can be stabilized against thermooxidative degradation by adding a combination of a sterically hindered phenol with an organic phosphite or phosphonite and a metal salt of a fatty acid.		

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Process for the stabilization of and stabilizer mixtures for recycled plastics

The invention relates to a process for the stabilization of recycled plastics, as predominantly produced in the household, in commerce or in industry and in useful material collections, and to the stabilizer mixtures which can be used for this purpose.

Recycling of waste is a problem of increasing importance for ecological reasons. The recycling of paper, textiles, glass or metals already takes place on a large scale, whether by separate collection or by sorting of the refuse. The recycling of plastic waste and used plastics is also an increasing aim. Thermoplastics are generally processed by re-melting.

However, the plastic waste produced in the household, in commerce or in industry or the plastic used for materials or used plastics obtained from collections or a return obligation, for example in specific sectors of industry, such as the automobile industry, electrical industry, agriculture or the packaging industry, predominantly comprises thermoplastics based on polyolefins, styrene polymers, polyvinyl chloride or polyethylene terephthalate.

Used plastics which are valuable raw materials can be obtained either as a single material or as a mixture. Single-material plastic waste can be produced directly in the production of plastic parts or obtained by separate collections.

On the other hand, the recycling of used plastics frequently means the use of a mixture of different types of plastic. Known industrial separation methods, for example hydrocyclone separation, mostly give only moderately clean fractions of various plastic mixtures, for example a mixture of polyolefins.

The use of plastic mixtures is associated with technical problems, since individual types of plastic have only restricted miscibility with one another, or none at all. Although various types of thermoplastics can be processed by melting and moulding, the resultant mixtures (polyblends) of immiscible plastics are inhomogeneous when considered microscopically, i.e. on a microscopic level they comprise different solid phases. This has a considerable adverse effect on the mechanical properties. Recyclates of this type can normally only be

used for purposes where relatively low strength requirements are made, for example as fillers or where thick-walled parts are used, for example noise protection dams.

Typical incompatible combinations which occur in domestic refuse are, for example, polyethylene and PVC or polyethylene and polystyrene or PET and polyolefins. In order to solve this problem, it has been proposed to add polymeric compatibilizers, also known as solid phase dispersants. Thus, for example, the addition of chlorinated polyethylene is capable of homogenizing mixtures of polyethylene and PVC. The addition of styrene-butadiene copolymers is capable of homogenizing mixtures of polyolefins and polystyrene. As a result of such a homogenization, the mechanical properties improve so much that these polyblends are also suitable for high-performance uses. A review of these developments is given by C. Sadrmohaghegh, G. Scott and E. Setudeh in *Polym. Plast. Technol. Eng.* 24 (1985), 149-185.

In an article which appeared in *Polymer Eng. and Science*, Vol. 17, pp. 700-705 (1977), the effect of small amounts of PVC and CPE on recycled polyethylene is studied, the authors observing that satisfactory stabilization of such recyclates is still not possible.

For the stabilization of recycled high-density polyethylene, P. Vink, R.T. Rotteveel and J.D.M. Wisse in *Polymer Degr. and Stability*, Issue 9, p. 133 (1984) studied various stabilizers from the classes of the phosphites, hindered phenols, benzotriazoles, hindered amines and phosphonites.

These authors also indicated that the recyclates must be re-stabilized. Although the plastics have mostly been treated originally with stabilizers against thermooxidative and in some cases also against photooxidative degradation, these stabilizers are lost during use of the plastics, during storage of the waste and during processing of the recyclates, in some cases due to migration, extraction or by degradation. Additionally, a recycled plastic generally differs structurally and also chemically from a new plastic as a consequence of the prior use or due to storage and processing; for example, sites of attack for oxidative degradation may already have formed. A recycled plastic therefore requires, for example, a relatively large amount of stabilizers or alternatively stabilizers which take into account these particular circumstances. The difficulty of finding suitable stabilizers is due to the specific type of previous damage/impurities, which may have taken place over an extended period.

- 3 -

Stabilization of a plastic mixture is likewise a difficult task, since each type of polymer makes specific requirements of the stabilizers. Thus, for example, completely different stabilizers are used for vinyl chloride polymers than for polyolefins or styrene polymers.

It would therefore be necessary to add a mixture of various stabilizers in order to stabilize a plastic mixture. In the case of complex plastic mixtures, this is a complicated method. In addition, various stabilizers can have adverse effects on one another or a stabilizer for one component can be damaging for the other component.

This problem has also been studied in the abovementioned literature and in Europ. Polym. J. 18 (1982), 1007, and the authors come to the conclusion that certain nickel complexes, in particular nickel dialkyldithiocarbamates, effect the best stabilization both against thermooxidative and against photooxidative degradation of polyethylene/polystyrene and polyethylene/polypropylene blends which have been homogenized by means of a compatibilizer. There is no mention therein of the stabilization of recyclates also containing PVC or of complex recycle mixtures.

It has now been found that both sorted and mixed recycled plastics can be stabilized in a simple and economical manner against thermooxidative degradation during processing and subsequent use by means of a mixture of stabilizers known per se.

The invention relates to a process for the stabilization of recycled plastics, predominantly thermoplastics, obtained from domestic, commercial and industrial waste or from useful material collections, which comprises adding from 0.01 to 10 % by weight of a mixture of a) at least one sterically hindered phenol, b) at least one organic phosphorus or phosphonous ester and c) at least one metal salt of a fatty acid to these plastics.

The a:b weight ratio is preferably from 20:1 to 1:20, particularly preferably from 10:1 to 1:10 and most preferably from 4:1 to 1:4. The (a+b):c weight ratio is preferably from 10:1 to 1:20, particularly preferably from 5:1 to 1:5 and most preferably from 3:1 to 1:3.

The plastics to be stabilized are, for example, used plastics from households and commerce (for example supermarkets), which predominantly originate from packaging materials. These can be, for example, films, bags, bottles and other containers or foams. Other materials may also be present. However, it is also possible for the above-described single-material plastics which have been previously damaged by use, storage or

- 4 -

processing to be stabilized. The materials originate, for example, from separation/sorting or from specific industrial sectors and return obligations, for example from the automobile industry, electrical/electronic industry, construction, agriculture and the textile industry.

The invention therefore relates to single-material recycled plastics, for example from the polymer classes consisting of the polyolefins and polystyrene, to defined recycled mixtures, known as polymer blends, and also to the stabilization of recycled plastic mixtures.

These mixtures of recycled plastic products predominantly comprise thermoplastics, for example polyolefins, polystyrene, polyvinyl chloride and engineering plastics, such as polyamides and polyesters. The recycled plastic mixtures predominantly comprise 25-100 % by weight, in particular 35-99 % by weight, of polyolefins, 0-25 % by weight of polystyrene, 0-25 % by weight of polyvinyl chloride and 0-25 % by weight of other thermoplastics, it also being possible for mixtures to be present within these groups of thermoplastics. Non-thermoplastics may also be present in the mixture in small amounts.

In particular, the invention relates to the stabilization of recycled plastic mixtures which comprise 55-95 % by weight of polyolefins, 5-25 % by weight of polystyrene, 0-15 % by weight of polyvinyl chloride and 0-10 % by weight of other thermoplastics.

In the case of single-material recyclates, the invention relates, in particular, to the stabilization of polyolefins and polystyrene. Particular preference is given to the stabilization of single-material polyolefin recyclates, for example polypropylene, high-density polyethylene, low-density polyethylene and polypropylene blends, and copolymers, such as PP/EPDM and PP/PE.

The invention furthermore relates to the stabilization of polyolefin mixtures which comprise virtually exclusively polyolefins of various structure.

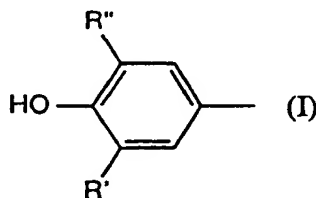
In plastic mixtures, the dominant polyolefins are usually polyethylene (PE) and polypropylene (PP), in particular low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE), furthermore copolymers such as ethylene-propylene (EPM) and ethylene-propylene-diene (EPDM) copolymers and ULDPE-MDPE. Polystyrene (PS and EPS) is also taken to mean copolymers containing styrene (for example ABS, ASA, HIPS and IPS), and polyvinyl chloride (PVC) is also

- 5 -

taken to mean copolymers predominantly comprising vinyl chloride (for example CPE). Of other thermoplastics, useful material collections principally contain polyethylene terephthalate (PET), and in addition polyamides, polycarbonate, cellulose acetate and polyvinylidene chloride. Secondary amounts, up to about 5 %, of non-thermoplastics, for example polyurethanes, formaldehyde resins and phenolic resins, and typical amino resins, and also elastomers, for example vulcanized or unvulcanized rubber, may also be present. In certain plastic wastes, small amounts of foreign substances, for example, paper, pigments and adhesives, which are frequently difficult to remove, may also be present. These foreign substances may also originate from contact with diverse substances during use or processing, for example fuel residues, paint components, traces of metal, initiator residues or traces of water.

From 0.05 to 5 % by weight of the mixture of a, b and c are preferably added to the recycle. From 0.1 to 2 % by weight of the mixture of a, b and c are particularly preferably added and most preferably from 0.1 to 0.5 % by weight of the mixture of a, b and c are added.

The sterically hindered phenols used as component a are known stabilizers against thermooxidative ageing of plastics, in particular polyolefins. These compounds preferably contain at least one group of the formula



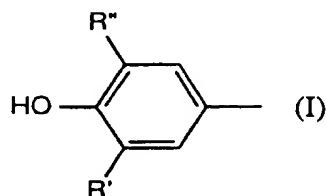
in which R' is hydrogen, methyl or tert-butyl; and R'' is unsubstituted or substituted alkyl or substituted thioether.

Examples of sterically hindered phenols of this type are:

2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-i-butylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-

methoxymethylphenol, 2,6-dinonyl-4-methylphenol, 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate and the calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate.

Component a is particularly preferably a compound containing at least one group of the formula

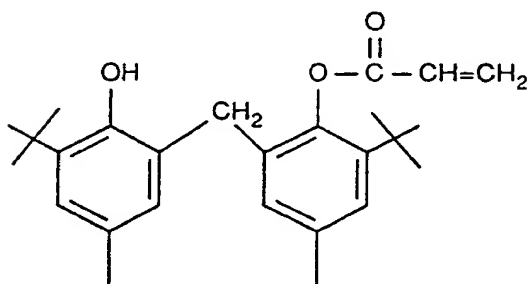


- 7 -

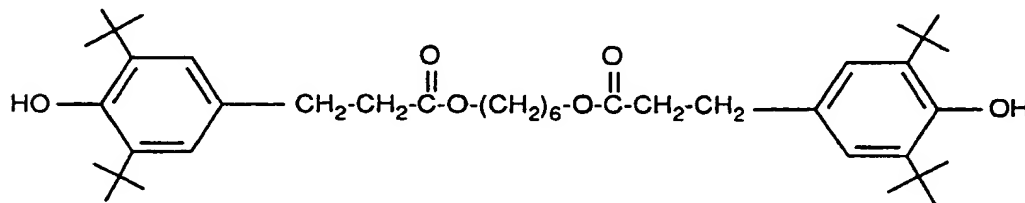
in which R' is methyl or tert-butyl; and R'' is unsubstituted or substituted alkyl or substituted thioether.

Examples of such hindered phenols are the esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid and of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with monohydric or polyhydric alcohols, for example with methanol, octadecanol, 1,6-hexanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxalamide, and the amides of these acids, for example N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)trimethylenediamine and N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)hydrazine.

Also particularly preferred are the following compounds:

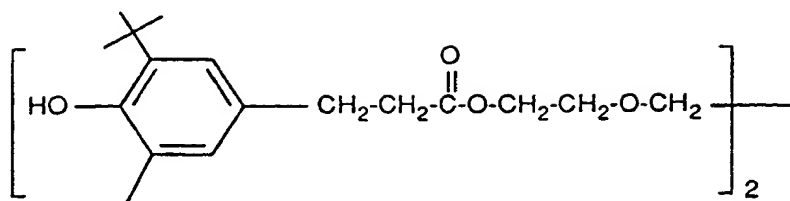


{2-propenoic acid 2-(1,1-dimethylethyl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]methyl]-4-methylphenylester};

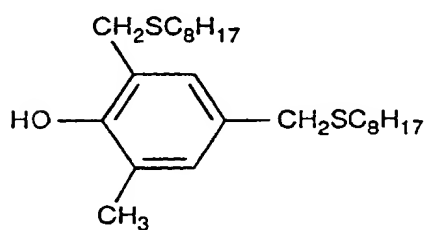


{benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-1,6-hexanediylester};

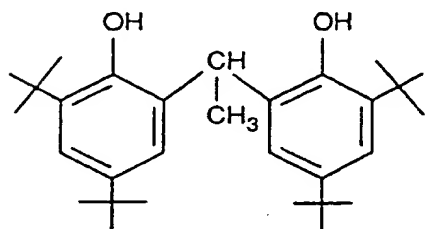
- 8 -



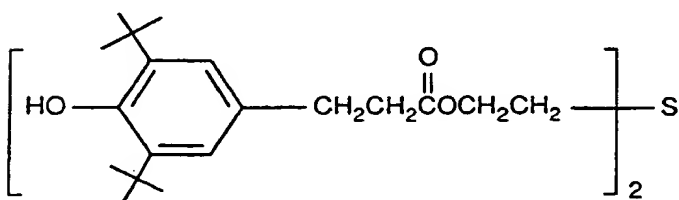
{ benzenepropanoic acid 3-(1,1-dimethylethyl)-4-hydroxy-5-methyl-1,2-ethanediylbis-(oxy-2,1-ethanediyl)ester};



{ 2-methyl-4,6-bis[(octylthio)methyl]-phenol};

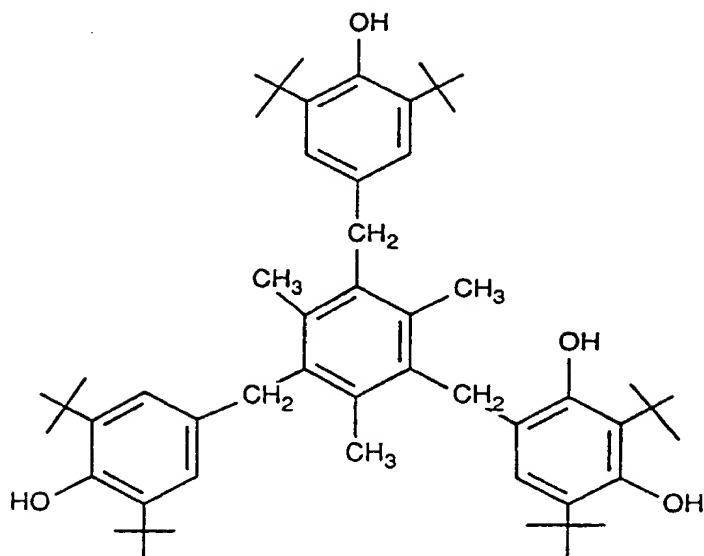


{ 2,2'-ethyldiene-bis-(4,6-di-tert.butylphenol)};

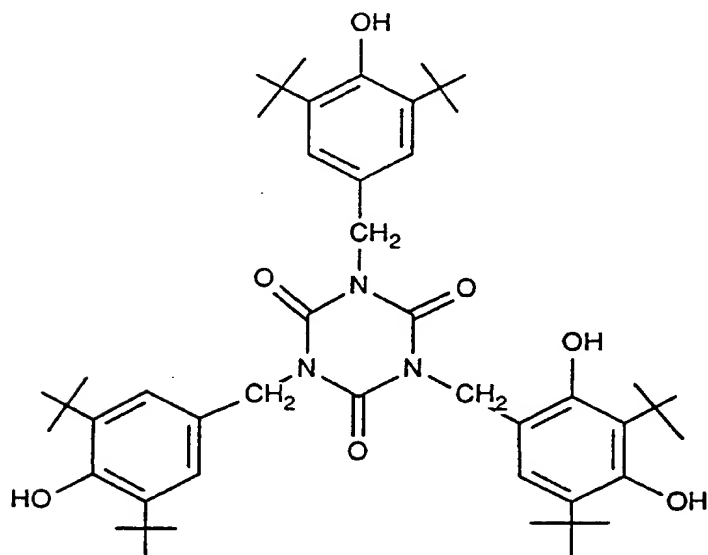


{ benzenepropanoic acid 3,5-bis(1,1-dimethylethyl)-4-hydroxy-thiodi-2,1-ethanediylester};

- 9 -



{4,4',4''-[(2,4,6-trimethyl-1,3,5-benzenetriyl)tris(methylene)]tris[2,6-bis(1,1-dimethylethyl)phenol]};



{1,3,5-tris[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-1,3,5-triazine-2,4,6(1H,3H,5H)-trione}.

Component a is most preferably a pentaerythritol ester or octadecyl ester of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid or 2,2'-ethylidenebis(4,6-di-tert-butylphenol).

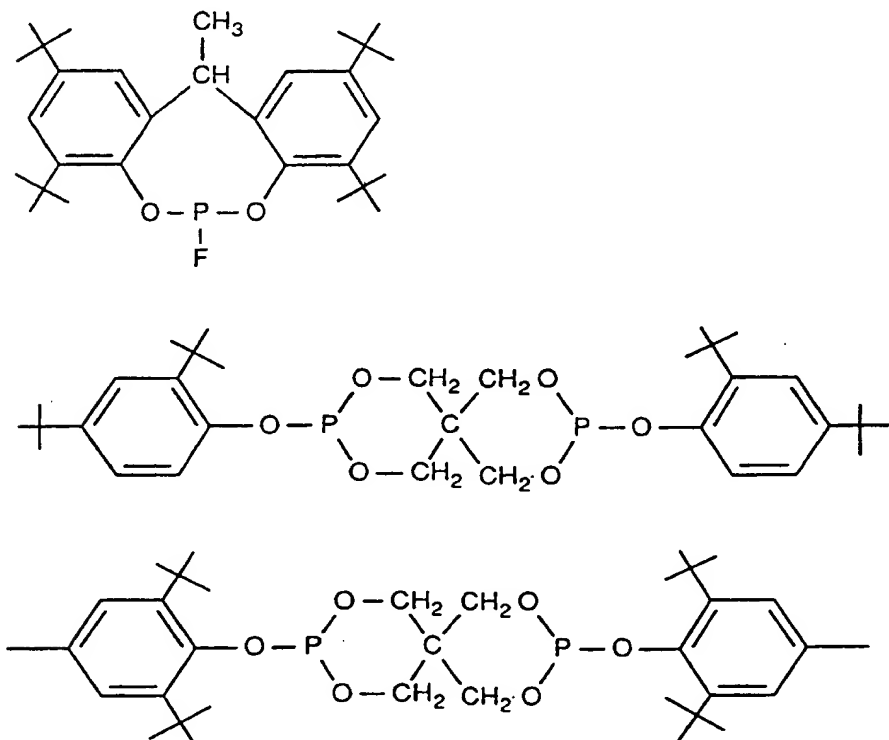
- 10 -

The organic phosphites and phosphonites used as component b are likewise known as stabilizers for plastics. They are used, in particular, as processing stabilizers for polyolefins.

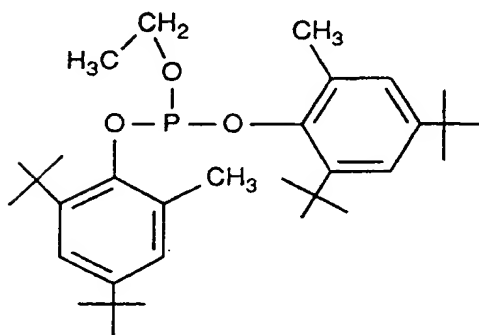
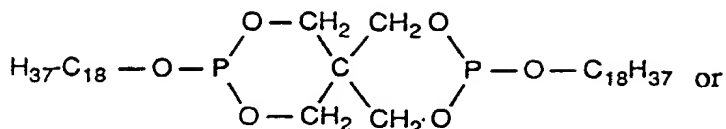
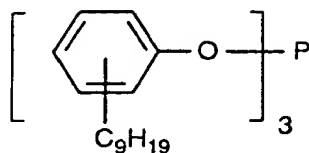
They are predominantly aromatic phosphites and phosphonites; for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythrityl diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, distearyl pentaerythrityl diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite, 3,9-bis(2,4-di-tert-butyl-4-methylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane, 3,9-tris(2,4,6-tris-tert-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane and 2,2'-ethyldienebis(4,6-di-tert-butylphenyl) fluorophosphite.

Preference is given to the following phosphites:

tris(2,4-di-tert-butylphenyl) phosphite;



- 11 -



Component b is most preferably tris(2,4-di-tert-butylphenyl) phosphite.

Component c is a metal salt of a fatty acid, in which the metal may be, in particular, an element of main or sub-group II or tin.

These are, in particular, zinc, magnesium, tin or preferably calcium salts from the series consisting of aliphatic saturated C₂-C₂₂carboxylates, aliphatic olefinic C₃-C₂₂carboxylates, aliphatic C₂-C₂₂carboxylates which are substituted by at least one OH group, cyclic or bicyclic C₅-C₂₂carboxylates, aromatic C₇-C₂₂carboxylates, aromatic C₇-C₂₂carboxylates which are substituted by at least one OH group, C₁-C₁₆alkyl-substituted phenylcarboxylates and phenyl C₁-C₁₆alkylcarboxylates, preference being given to stearates, laurates and behenates.

Component c is very particularly preferably calcium stearate, zinc stearate or magnesium stearate.

It is also possible to use a mixture of various components a, b and c. For example, component c may be a mixture of calcium laurate and calcium stearate or of zinc stearate

and calcium stearate.

The present invention furthermore relates to stabilizer mixtures and to the use thereof for recycled mixtures of predominantly thermoplastics obtained from domestic, commercial and industrial waste, useful material collections and used plastics, these stabilizer mixtures comprising a) at least one sterically hindered phenol, b) at least one organic phosphorous or phosphonous ester and c) at least one metal salt of a fatty acid.

Most preferred are stabilizer mixtures comprising per 100 parts

- (A) as component a) 5-50 parts of pentaerythritol ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 5-50 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 5-50 parts calcium stearate;
- (B) as component a) 5-50 parts of pentaerythritol ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 5-50 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 5-50 parts of a mixture of calcium and zinc stearates;
- (C) as component a) 5-50 parts of octadecyl ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 5-50 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 5-50 parts of calcium stearate; or
- (D) as component a) 10-40 parts of pentaerythritol ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 10-40 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 20-50 parts of calcium stearate.

The present invention furthermore relates to recycled mixtures of predominantly thermoplastics obtained from domestic, commercial and industrial waste, useful material collections and used plastics, which mixtures contain a) at least one sterically hindered phenol, b) at least one organic phosphorous or phosphonous ester and c) at least one metal salt of a fatty acid.

Preferred recycled mixtures of predominantly thermoplastics, preferred stabilizer mixtures and their use conform in their components and mixing ratios to the preferences described in greater detail under the process.

- 13 -

The addition of these combinations to the recyclate allows thermoplastic processing with reduced degradation and/or extends the service life of the materials produced from the recyclate. This is true irrespective of whether a compatibilizer is added to the recyclate or not. However, the addition of the combination of a, b and c is of particular significance for recyclates to which is added a polymer or polymer mixture which increases the compatibility of the individual plastics with one another, since this polymer generally also requires stabilization.

Further conventional plastic additives can also be polymers which improve the material properties of the previously damaged plastic, for example elastomers (impact modifiers) and compatibilizers. Impact modifiers are homopolymers or copolymers which are able to modify brittle polymers so that they remain tough even at low temperatures. EP(D)M polymers, ABR, BR and SBR graft polymers, inter alia, are suitable for this purpose.

The compatibilizers can be, for example, copolymers, in particular block copolymers, of styrene with butadiene and, if desired, acrylonitrile. They can be copolymers of ethylene and propylene, and may contain a third monomer component, for example butadiene.

Chlorinated polyethylene or ethylene-vinyl acetate copolymers are also suitable as compatibilizers, naturally depending on the particular composition of the recyclate.

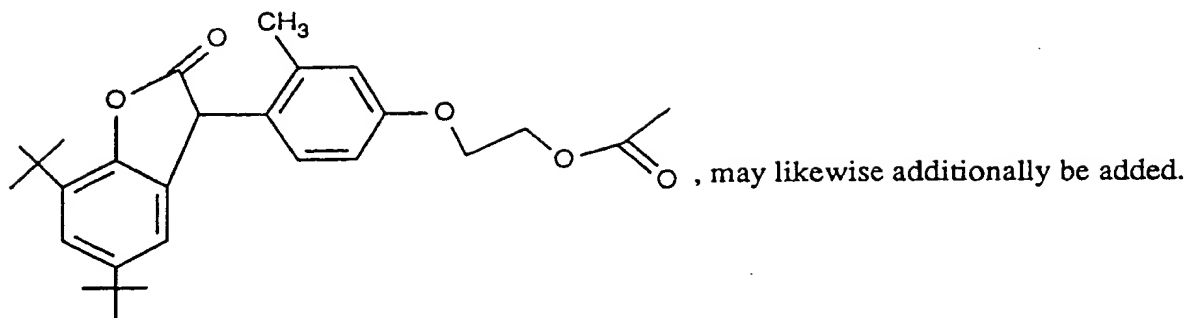
Further suitable compatibilizers contain, in particular, polar groups, eg maleic anhydride-styrene copolymers or graft polymers containing acrylic acid groups.

The polymeric compatibilizers are generally used in amounts of 2-20 % by weight, based on the plastic to be stabilized.

The stabilizing action of the mixture of a, b and c, in particular the long-term stability, may be synergistically increased by the addition of so-called thiosynergists. These are aliphatic thioethers, in particular esters of thiodipropionic acid. Examples are the lauryl, stearyl, myristyl and tridecyl esters of thiodipropionic acid or distearyl disulfide. These thiosynergists are preferably used in an amount of from 0.1 to 1 % by weight, based on the recyclate.

Further suitable stabilizers from the series consisting of the lactates, eg. calcium lactate or calcium stearoyl-2-lactylate, or lactones, eg.

- 14 -



If high light stability is also required of the article produced from the recycle, the addition of one or more light stabilizers is advisable. Suitable light stabilizers are, in particular, those from the series consisting of the benzophenones, benzotriazoles, oxanilides and sterically hindered amines. Examples of such compounds are:

2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2-(2'-Hydroxyphenyl)benzotriazoles, for example the 5'-methyl, 3',5'-di-tert-butyl, 5'-tert-butyl, 5'-(1,1,3,3-tetramethylbutyl), 5-chloro-3',5'-di-tert-butyl, 5-chloro-3'-tert-butyl-5'-methyl, 3'-sec-butyl-5'-tert-butyl, 4'-octoxy, 3',5'-di-tert-amyl and 3',5'-bis(α,α -dimethylbenzyl) derivatives.

Oxalamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyloxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and mixtures thereof with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide, and mixtures of o- and p-methoxy- and of o- and p-ethoxy-disubstituted oxanilides.

Sterically hindered amines, for example bis(2,2,6,6-tetramethylpiperidyl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl) sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the product of the condensation of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the product of the condensation of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine or

- 15 -

4-morpholino-2,6-dichloro-1,3,5-triazine, tetrakis(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetracarboxylate, bis(2,2,6,6-tetramethylpiperidyl) succinate, N-(1,2,2,6,6-pentamethyl-4-piperidyl)- α -dodecylsuccinimide, N-(2,2,6,6-tetramethyl-4-piperidyl)- α -dodecylsuccinimide, 2,4,6-tris[N-pentyl-2-(3,3,5,5-tetramethyl-2-oxo-piperazino)ethylamino]-1,3,5-triazine, 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-21-oxo-dispiro[5,1,11,2]heneicosane, 2,2,4,4-tetramethyl-20-(2-dodecyloxycarbonyl)ethyl-7-oxa-3,20-diaza-21-oxo-dispiro[5,1,11,2]heneicosane, 8-acetyl-3-dodecyl-1,3,8-triaza-7,7,9,9-tetramethylspiro[4,5]decane-2,4-dione, 1,5,8,12-tetrakis[2,4-bis(N-butyl-1,2,2,6,6-pentamethyl-4-piperidylamino)-1,3,5-triazin-6-yl]-1,5,8,12-tetraazadodecane, and polysiloxanes containing 2,2,6,6-tetramethyl-4-piperidinyl groups.

The light stabilizers are preferably added in an amount of from 0.01 to 2 % by weight, in particular from 0.05 to 0.5 % by weight, based on the plastic mixture. The light stabilizer used is preferably a combination of a benzotriazole with a sterically hindered amine.

The mixtures according to the invention as well as the additives mentioned can be added to the recyclate in compact, extruded form or on a support material, or directly as a mixture or in the form of powders.

If required, further conventional plastic additives can be added to the recycled plastic, for example fillers, such as sawdust or mica, reinforcing agents, such as glass fibres, glass beads or mineral fibres, pigments, plasticizers, lubricants, flameproofing agents, antistatics or blowing agents. These additives depend on the intended use of the recyclate.

The recyclates stabilized in this way can be used for a very wide variety of applications, for example for tubes, profiles, sheets, cable insulations, sports equipment, garden furniture, films, construction parts, parts of vehicles and machines and containers of all types, for example bottles.

The recyclate can also be mixed with new plastics or employed together with new plastics, for example in a coextrusion process.

The examples below illustrate the novel process and stabilizer mixture in greater detail. As in the remainder of the description, parts are parts by weight and percentages are per cent by weight, unless otherwise stated.

- 16 -

Example 1: Used plastic material (PP copolymer from used battery casings) in the form of granules are homogenized with the stabilizers (Table 1) in a screw mixer and subsequently extruded five times one after the other in a twin-screw compounder (temperature 260°C). The melt flow index (MFI, 230°C, 2.16 kg) is determined before the extrusions and after the 1st, 3rd and 5th extrusions in accordance with DIN 53 735M (ISO 1133/12).

The granules are subsequently converted into sheets (thickness 2 mm) at 240°C in an injection-moulding machine (Arburg 100). These sheets are subjected to artificial weathering at 135°C in a fan-assisted oven until they become brittle (Table 2).

Table 1:

	Stabilizer mixture	Melt flow index after			
		0	1st	3rd	5th extrusion
--	without stabilizer	10.6	14.6	18.7	25.2
Ex. 1	0.06 % AO-1 + 0.14 % P-1 + 0.13 % F-1	10.6	13.2	15.6	17.8

The sample stabilized according to the invention exhibits only a slight increase in melt flow index after repeated extrusion. Due to degradation reactions and decomposition of the polymer (chain breaking), the melt flow index increases.

Table 2: Heat ageing of PP from battery casings

	Stabilizer mixture	Days to embrittlement
--	without stabilizer	14
Ex. 1a	0.06 % AO-1 + 0.14 % P-1 + 0.13 % F-1	50

Examples 2-5: Used plastic material (BOPP: agglomerated production waste from biaxially oriented polypropylene) in the form of granules is homogenized with the stabilizers (Table 2) in a screw mixer and subsequently extruded five times one after the other in a twin-screw compounder (temperature 230°C). The melt flow index (MFI, 230°C, 2.16 kg) is determined after the 1st, 3rd and 5th extrusions in accordance with DIN 53 735 M (ISO 1133/12).

Table 3: Repeated extrusion of BOPP

	Stabilizer mixture	Melt flow index after		
		1st	3rd	5th extrusion
--	without stabilizer	6.0	7.1	8.3
Ex. 2	0.04 % AO-1 + 0.08 % P-1 + 0.08 % F-1	5.6	5.8	6.4
Ex. 3	0.08 % AO-1 + 0.16 % P-1 + 0.16 % F-1	5.5	5.9	6.0
Ex. 4	0.08 % AO-2 + 0.16 % P-1 + 0.16 % F-1	5.7	6.0	6.5
Ex. 5	0.08 % AO-3 + 0.16 % P-1 + 0.16 % F-1	5.7	6.0	6.5

The samples stabilized according to the invention exhibit only a slight increase in the melt flow index after repeated extrusion. Due to degradation reactions and decomposition of the polymer (chain breaking), the melt flow index increases.

The granules are subsequently converted into test specimens (thickness 2 mm) at 230°C in an injection-moulding machine (Arburg 100). These test specimens are subjected to heat ageing at 135°C in a fan-assisted oven until they become brittle (Table 4).

Table 4: Heat ageing (flexural test) of BOPP

	Stabilizer mixture	Days before embrittlement
--	without stabilizer	54
Ex. 2 a	0.04 % AO-1 + 0.08 % P-1 + 0.08 % F-1	92

Further test specimens are stored at 135°C in a fan-assisted drying cabinet. 5 test specimens are taken after 500 hours, 1000 hours, 1500 hours and 2000 hours in order to determine the tensile impact strength in accordance with DIN 53448 (Table 5).

Table 5: Tensile impact strength of BOPP after heat ageing

	Stabilizer mixture	Tensile impact strength (kJ/m ²) after			
		500 h	1000 h	1500 h	2000 h
--	without stabilizer	644	480	0	0
Ex. 2 b	0.04 % AO-1 + 0.08 % P-1 + 0.08 % F-1	607	669	643	634

Examples 6-8: Used BOPP material (biaxially oriented PP production waste) in the form of granules is homogenized with the stabilizers (Table 6) in a screw mixer and subsequently extruded once in a twin-screw compounder. The granules are subsequently converted into test specimens at 230°C in an injection-moulding machine (Arburg 100). For exposure testing, these test specimens are stored in an Atlas Ci 65 A Weather-O-Meter. 5 test specimens are taken after UV exposure for 500 hours, 1000 hours, 1500 hours and 2000 hours in order to determine the tensile impact strength in accordance with DIN 53448.

Table 6: Tensile impact strength of BOPP after artificial weathering in a Weather-O-Meter

	Stabilizer mixture	Tensile impact strength (kJ/m ²) after weathering in the WOM			
		0 h	1000 h	1500 h	2000 h
--	without stabilizer	278	37	-	-
Ex. 6	0.01 % AO-1 + 0.02 % P-1 + 0.08 % F-1 + 0.06 % LS-1 + 0.03 % LS-2	332	329	330	274
Ex. 7	0.02 % AO-1 + 0.04 % P-1 + 0.16 % F-1 + 0.12 % LS-1 + 0.06 % LS-2	301	323	326	297
Ex. 8	0.03 % AO-1 + 0.06 % P-1 + 0.24 % F-1 + 0.18 % LS-1 + 0.09 % LS-2	253	364	331	304

Example 9: Used HDPE material (drum goods) in the form of granules is homogenized

- 19 -

with the stabilizers (Table 7) in a screw mixer and subsequently extruded five times one after the other in a twin-screw compounder (ZSK) at 230°C. The melt flow index (MFI, 230°C/10 kg) is determined after the 1st, 3rd and 5th extrusions in accordance with DIN 53735 M (ISO 1133/12).

Table 7: Used HDPE material (drum goods), repeated extrusion

	Stabilizer mixture	Melt flow index after		
		1st	3rd	5th extrusion
--	without stabilizer	0.67	0.46	0.37
Ex. 9	0.04 % AO-1 + 0.08 % P-1 + 0.08 % F-1	0.70	0.68	0.69

Extrusion: ZSK, 230 °C, 100 rpm

The sample stabilized according to the invention exhibits no drop in melt flow index after repeated extrusion. Due to crosslinking of the polymer, the melt flow index of the sample which has not subsequently been stabilized drops.

Examples 10-22: Used plastic material (average composition: HDPE/PP = 90/10, originating from hollow articles) is extruded with the stabilizers (Table 8) at 240°C. The granules are subsequently converted into sheets (thickness 2 mm) at 220°C in an injection-moulding machine (Arburg 100). These test specimens are subjected to artificial weathering at 120°C in a fan-assisted oven until they become brittle.

Further test specimens are stored at 120°C in a fan-assisted drying cabinet. 5 test specimens are taken after 500 hours, 1000 hours and 1500 hours in order to determine the tensile impact strength (Table 9) in accordance with DIN 53448.

Table 8: Artificial weathering (flexural test) of polyolefin mixtures (HDPE/PP = 90/10)

	Stabilizer mixture	Days before embrittlement
--	without stabilizer	37
Ex. 10	0.04 % AO-1 + 0.08 % P-1 + 0.08 % F-1	87
Ex. 11	0.08 % AO-1 + 0.16 % P-1 + 0.16 % F-1	109
Ex. 12	0.16 % AO-1 + 0.08 % P-1 + 0.16 % F-1	68
Ex. 13	0.04 % AO-2 + 0.08 % P-1 + 0.08 % F-1	> 84
Ex. 14	0.08 % AO-2 + 0.16 % P-1 + 0.16 % F-1	> 84
Ex. 15	0.04 % AO-3 + 0.08 % P-1 + 0.08 % F-1	> 84
Ex. 16	0.08 % AO-3 + 0.16 % P-1 + 0.16 % F-1	> 84
Ex. 17	0.04 % AO-1 + 0.08 % P-1 + 0.08 % F-2	> 84
Ex. 18	0.08 % AO-1 + 0.16 % P-1 + 0.16 % F-2	> 84
Ex. 19	0.04 % AO-1 + 0.08 % P-1 + 0.05 % F-1 + 0.03 % F-2	> 84
Ex. 20	0.08 % AO-1 + 0.16 % P-1 + 0.10 % F-1 + 0.06 % F-2	> 84
Ex. 21	0.04 % AO-1 + 0.08 % P-1 + 0.018 % F-1 + 0.027 % F-2 + 0.035 % Z-1	> 84
Ex. 22	0.08 % AO-1 + 0.16 % P-1 + 0.036 % F-1 + 0.054 % F-2 + 0.070 % Z-1	> 84

Table 9: Tensile impact strength of polyolefin mixtures after heat ageing

	Stabilizer mixture	Tensile impact strength (kJ/m ²) after		
		500 h	1000 h	1500 h
--	without stabilizer	777	37	-
Ex. 10a	0.04 % AO-1 + 0.08 % P-1 + 0.08 % F-1	954	961	914
Ex. 11a	0.08 % AO-1 + 0.16 % P-1 + 0.16 % F-1	870	980	800
Ex. 12a	0.16 % AO-1 + 0.08 % P-1 + 0.16 % F-1	> 1250	1178	> 1250

Examples 23 and 24: A mixture of 36.14 g of BOPP film granules, 0.029 g of AO-1, 0.014 g of P-1 and 0.029 g of F-1 (or 0.014 g of AO-1, 0.029 g of P-1 and 0.029 g of F-1 in the case of Example 24) is compounded for 30 minutes at 200°C under nitrogen in a Brabender mixing chamber (Brabender Plasticorder PL 2001/3, W50 mixing chamber). At the same time, the change in torque, i.e. the force necessary to rotate the compounding blades, is recorded (Table 10).

After a mixing time of 30 minutes, the polymer melt is removed from the Brabender chamber and pressed at 200°C to give sheets 2 mm thick. Test specimens are stamped out of these sheets and used to determine the tensile impact strength in accordance with DIN 54 448 on unnotched test specimens (Table 10).

The melt flow index (MFI, 230°C, 2.16 kg) is determined on fragments of the above sheets in accordance with DIN 53 735M (ISO 1133/12) (Table 10).

Table 10:

	Torque [Nm] after a mixing time of					Tensile impact strength [kJ/m ²]	Melt flow index [g/10 min]
	2	5	10	20	30 min		
without stab.	9.2	7.1	6.4	4.8	3.7	74	30.8
Ex. 23	8.5	7.3	6.8	6.5	5.5	167	13.5
Ex. 24	8.4	7.3	6.7	6.3	5.3	115	15.0

The samples stabilized according to the invention exhibit a slight drop in torque, high

- 22 -

tensile impact strength and low melt flow index compared with the sample without stabilizers. Due to degradation reactions and decomposition of the polymer (chain breaking), the torque drops and the melt flow index increases.

Examples 25-40: For the analyses with mixed plastic, a used plastic mixture of the composition

80 % of PO lightweight fraction
15 % of PS
2 % of PET
3 % of PVC

is used

39 g of the used plastic mixture are compounded for 10 minutes in a Brabender W 50 mixing chamber held at 200°C (40 rpm). The additives (Table 11) are introduced into the mixing chamber right at the beginning together with the plastic mixture. After 10 minutes, the mixing is stopped, and the polymer material is removed from the mixing chamber and pre-pressed for 1 minute at about 20 kN at 30°C.

Sheets with a thickness of 2 mm are produced from this pressing at 200°C/50 kN.

Test specimens are stamped out of these sheets and aged at 110°C in a fan-assisted oven. The ageing is continued until the samples become brittle, which is checked by a flexural test. The results of the heat ageing are shown in Table 11.

Table 11

Heat ageing at 110°, flexural test

mixed plastics (80 % of PO, 15 % of PS, 2 % of PET, 3 % of PVC)

	%	Additive	Days before embrittlement
--	--	none	4
Ex. 25	0.02/0.06/0.12	F-1 / AO-1 / P-1	27
Ex. 26	0.08/0.06/0.06	F-1 / AO-1 / P-1	18
Ex. 27	0.08/0.096/0.024	F-1 / AO-1 / P-1	16
Ex. 28	0.16/0.12/0.12	F-1 / AO-1 / P-1	18
Ex. 29	0.16/0.192/0.048	F-1 / AO-1 / P-1	21
Ex. 30	0.16/0.048/0.192	F-1 / AO-1 / P-1	14
Ex. 31	0.04/0.12/0.24	F-1 / AO-1 / P-1	24
Ex. 32	0.08/0.04/0.08	F-1 / AO-1 / P-1	9
Ex. 33	0.16/0.08/0.16	F-1 / AO-1 / P-1	23
Ex. 34	0.08/0.04/0.08	F-2 / AO-1 / P-1	12
Ex. 35	0.08/0.04/0.08	F-3 / AO-1 / P-1	16
Ex. 36	0.02/0.06/0.12	F-1 / AO-2 / P-1	19
Ex. 37	0.08/0.096/0.024	F-1 / AO-2 / P-1	12
Ex. 38	0.08/0.024/0.096	F-1 / AO-2 / P-1	12
Ex. 39	0.16/0.12/0.12	F-1 / AO-2 / P-1	14
Ex. 40	0.16/0.192/0.048	F-1 / AO-2 / P-1	19
Ex. 41	0.04/0.12/0.24	F-1 / AO-2 / P-1	17

10 min Brabender 200°C

2 mm pressed sheet

Examples 41-44: 7.5 parts of a compatibilizer based on S(EB)S block copolymer are added to the used plastic mixture.

The procedure is analogous to Example 25.

The results are shown in Table 12.

Table 12

Artificial ageing at 110°, flexural test
mixed plastics (80 % of PO, 15 % of PS, 2 % of PET, 3 % of PVC)
7.5 % of compatibilizer (based on S(EB)S block copolymer)

	%	Additive	Days before embrittlement
--	--	none	4
Ex. 41	0.08/0.04/0.08	F-1 / AO-1 / P-1	9
Ex. 42	0.08/0.04/0.08/0.2	F-1 / AO-1 / P-1 / T-1	37
Ex. 43	0.06/0.03/0.06/0.05	F-1 / AO-1 / P-1 / AO-2	20
Ex. 44	0.08/0.8/0.4	F-1 / P-1 / AO-3	11

10 min Brabender 200°C

2 mm pressed sheet

Examples 45-47: 45 g of EPS recyclate (granules) are compounded for 10 minutes in a Brabender W 50 mixing chamber held at 200°C (40 rpm). The additives (Table 13) are introduced into the mixing chamber right at the beginning together with the plastic mixture. After 10 minutes, the mixing is stopped, and the polymer material is removed from the mixing chamber and pre-pressed for 1 minute at about 20 kN at 30°C.

Sheets with a thickness of 2 mm are produced from this pressing at 200°C/50 kN.

The melt volume index is determined from this pressing after comminution.

The samples stabilized according to the invention exhibit only a slight increase in melt volume index (Table 13) compared to the non-stabilized sample.

- 25 -

Table 13

Brabender experiment (20 min, 220°C, 40 rpm)
using EPS recyclate from packaging (granules)

	%	Additive	MVI (200/5)
--	--	none	56.8
Ex. 45	0.08/0.04/0.08	F-1 / AO-1 / P-1	44.6
Ex. 46	0.08/0.04/0.08	F-1 / AO-2 / P-1	44.5
Ex. 47	0.08/0.04/0.06	F-1 / AO-4 / P-1	39.0

Examples 48 and 49: 36 g of used LDPE are compounded for 10 minutes in a Brabender W 50 mixing chamber held at 200°C (40 rpm). The additives (Table 14) are introduced into the mixing chamber right at the beginning together with the plastic mixture. After 10 minutes, the mixing is stopped, and the polymer material is removed from the mixing chamber and pre-pressed for 1 minute at about 20 kN at 30°C.

Sheets with a thickness of 2 mm are produced from this pressing at 200°C/50 kN.

Test specimens are stamped out of these sheets and aged at 110°C in a fan-assisted oven. The ageing is continued until the samples become brittle, which is checked by a flexural test. The results of the artificial ageing are shown in Table 14.

Table 14

Heat ageing at 110°, flexural test

Used LDPE

	%	Additive	Days before embrittlement	OIT [min]
--	--	none	7	3
Ex. 48	0.08/0.04/0.08	F-1 / AO-1 / P-1	> 70	8
Ex. 49	0.16/0.08/0.16	F-1 / AO-1 / P-1		19

10 min Brabender 200°C

2 mm pressed sheet

OIT: Oxygen Induction Time, at 200°C, in accordance with ASTM D 3895-80, heating rate 10°C/min

Examples 50-52: A PP/LDPE agglomerate is used for the testing. A compatibilizer is added to this agglomerate.

Comp. = compatibilizer (based on PE grafted with maleic anhydride).

36.7 g of the mixture of agglomerate and compatibilizer are compounded for 10 minutes in a Brabender W 50 mixing chamber held at 200°C (40 rpm). The additives (Table 15) are introduced into the mixing chamber right at the beginning together with the plastic mixture. After 10 minutes, the mixing is stopped, and the polymer material is removed from the mixing chamber and pre-pressed for 1 minute at about 20 kN at 30°C.

Sheets with a thickness of 2 mm are produced from this pressing at 200°C/50 kN and the tensile impact strength in accordance with DIN 53448 is determined.

The melt volume index is determined from this pressing after comminution.

- 27 -

Brabender analysis (200°C, 40 rpm, 10 min)
 PP/LDPE agglomerate (50/50)
 Comp. = compatibilizer
 (Based on PE grafted with maleic anhydride)

	%	Additive	MVI (190/2.16)	Tensile impact strength [kJ/m ²]
--	--	none	22.39	60
Ex. 50	2.5/0.08/0.04/0.08	Comp./ F-1 / AO-1 / P-1	16.85	106
Ex. 51	5.0/0.08/0.04/0.08	Comp./ F-1 / AO-1 / P-1	12.70	135
Ex.52	7.5/0.08/0.04/0.08	Comp./ F-1 / AO-1 / P-1	9.70	153

2 mm pressed sheet

The following stabilizers are used:

AO-1 Pentaerythritol ester of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid

AO-2 Octadecyl ester of β -(3,5-di-tert.butyl-4-hydroxyphenyl)-propionic acid

AO-3 2,2'-ethylidene-bis-(4,6-di-tert.butyl-phenol)

AO-4 benzenepropionic acid 3-(1,1-dimethylethyl)-4-hydroxy-5-methyl-1,2-ethanediylbis(oxy-2,1-ethanediyl)ester

F-1 calcium stearate

F-2 zinc stearate

F-3 magnesium stearate

LS-1 5-chloro-3',5'-di-tert.butyl-2(2'-hydroxyphenyl)-benzotriazole

LS-2 bis-(2,2,6,6-tetramethylpiperidyl)-sebacate

P-1 tris-(2,4-di-tert.butylphenyl) phosphite

T-1 3,3'-thiobispropionic acid-dioctadecyl ester

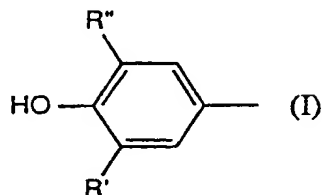
Z-1 pentaerythritol

WHAT IS CLAIMED IS:

1. A process for the stabilization of recycled plastics, predominantly thermoplastics, obtained from domestic, commercial and industrial waste or from useful material collections, which comprises adding from 0.01 to 10 % by weight of a mixture of a) at least one sterically hindered phenol, b) at least one organic phosphorous or phosphonous ester and c) at least one metal salt of a fatty acid to these plastics.
2. A process according to claim 1, wherein the a:b weight ratio is from 20:1 to 1:20 and the (a+b):c weight ratio is from 10:1 to 1:20.
3. A process according to claim 1, wherein the a:b weight ratio is from 10:1 to 1:10 and the (a+b):c weight ratio is from 5:1 to 1:5.
4. A process according to claim 1, wherein the recycled plastics are in the form of a mixture which comprises 25-100 % by weight of polyolefins, 0-25 % of polystyrene, 0-25 % of polyvinyl chloride and 0-25 % of other thermoplastics.
5. A process according to claim 1, wherein the recycled plastics are in the form of a mixture which comprises 55-95 % by weight of polyolefins, 5-25 % of polystyrene, 0-15 % of polyvinyl chloride and 0-10 % of other thermoplastics.
6. A process according to claim 1, wherein the recycled plastics are in the form of single-material recyclates from the series consisting of the polyolefins and polystyrene.
7. A process according to claim 1, wherein the recycled plastics are in the form of polypropylene recyclates and corresponding copolymers.
8. A process according to claim 1, wherein the recycled plastics are in the form of polyethylene recyclates.
9. A process according to claim 1, wherein the recycled plastics are in the form of polyolefin mixtures from industrial separation processes.
10. A process according to claim 1, wherein from 0.05 to 5 % by weight of the mixture of a, b and c is added to the recycled plastic.

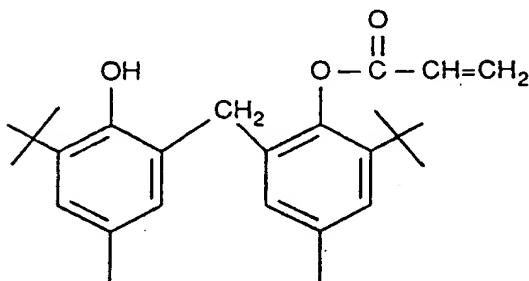
- 29 -

11. A process according to claim 1, wherein component a is a compound containing at least one group of the formula

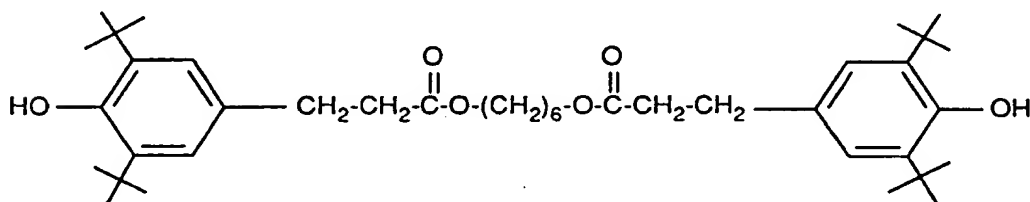


in which R' is hydrogen, methyl or tert-butyl; and R'' is unsubstituted or substituted alkyl or substituted thioether.

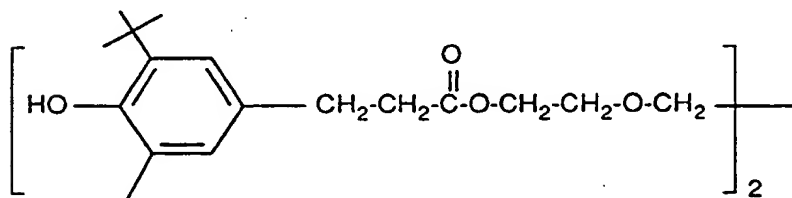
12. A process according to claim 1, wherein component a is a compound selected from the group consisting of



{2-propenoic acid 2-(1,1-dimethylethyl)-6-[[3-(1,1-dimethylethyl)-2-hydroxy-5-methylphenyl]methyl]-4-methylphenylester};



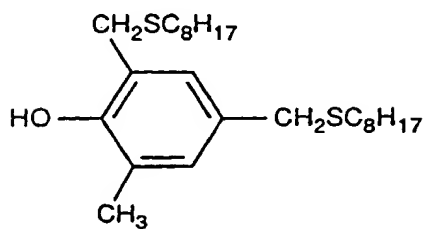
{benzenepropanoic acid 3,5-bis(1,1-dimethyl-ethyl)-4-hydroxy-1,6-hexanediylester};



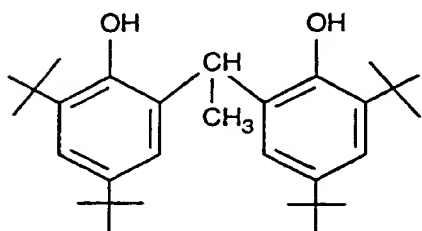
{benzenepropanoic acid 3-(1,1-dimethylethyl)-4-hydroxy-5-methyl-1,2-ethanediylbis-

- 30 -

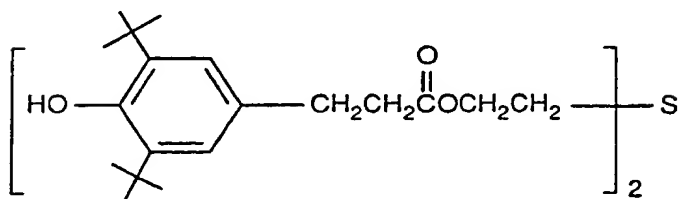
(oxy-2,1-ethanediyl)ester);



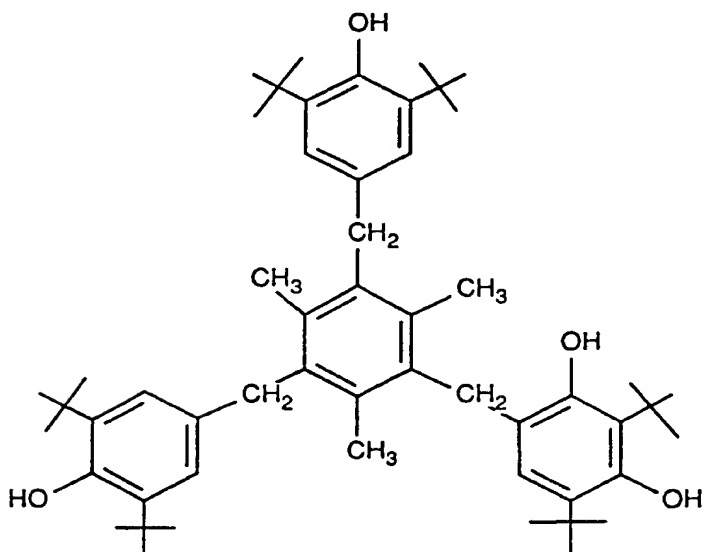
{2-methyl-4,6-bis[(octylthio)methyl]-phenol};



{2,2'-ethylidene-bis-(4,6-di-tert-butylphenol)};

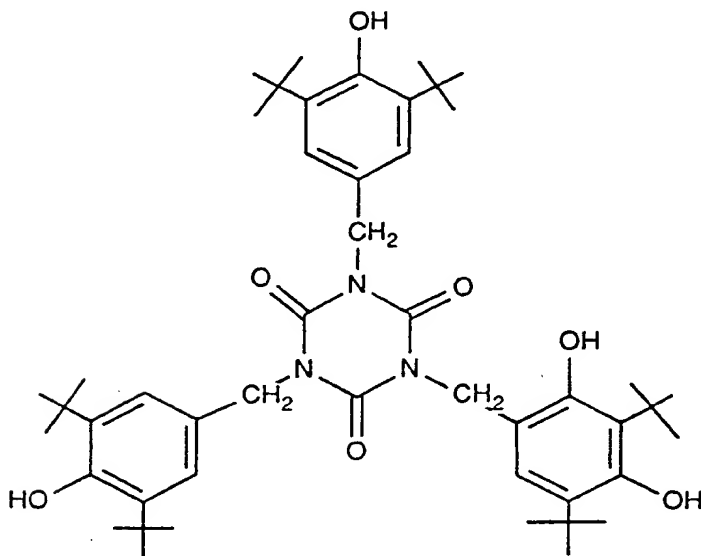


{benzenepropanoic acid 3,5-bis(1,1-dimethylethyl)-4-hydroxy-thiodi-2,1-ethanediylester};



- 31 -

{4,4',4''-[(2,4,6-trimethyl-1,3,5-benzenetriyl)tris-(methylene)]tris[2,6-bis(1,1-dimethylethyl)phenol]};



{1,3,5-tris[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-1,3,5-triazine-2,4,6(1H,3H,5H)-trione}; and
the pentaerythritol ester or the octadecyl ester of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid.

13. A process according to claim 1, wherein component a is the pentaerythritol ester or the octadecyl ester of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid or 2,2'-ethyldiene-bis-(4,6-di-tert-butylphenol).

14. A process according to claim 1, wherein component b is an aromatic phosphite.

15. A process according to claim 1, wherein component b is tris(2,4-di-tert-butylphenyl) phosphite.

16. A process according to claim 1, wherein component c is a metal salt of a fatty acid, in which the metal is an element of main or sub-group II or tin.

17. A process according to claim 1, wherein component c is magnesium stearate or laurate, tin stearate or laurate, zinc stearate or laurate or calcium stearate or laurate.

- 32 -

18. A process according to claim 1, wherein component c is calcium stearate or zinc stearate.

19. A process according to claim 1, wherein component c is a mixture of various metal stearates, in which the metal is an element of main or sub-group II or tin.

20. A process according to claim 1, wherein the plastic recyclate additionally contains a polymer or polymer mixture which increases the compatability of the individual plastics with one another.

21. A process according to claim 1, wherein the plastic recyclate additionally contains a polymer or polymer mixture in an amount of 2-20 % by weight, based on the plastic recyclate mixture, which increases the compatability of the individual plastics with one another.

22. A process according to claim 1, wherein a thiosynergist from the series consisting of the esters of thiodipropionic acid is additionally added to the plastic recyclate.

23. A process according to claim 1, wherein a thiosynergist from the series consisting of the esters of thiodipropionic acid is additionally added in an amount of from 0.1 to 1 % by weight, based on the plastic recyclate, to the plastic recyclate.

24. A process according to claim 1, wherein at least one light stabilizer from the series consisting of the benzophenones, benzotriazoles, oxanilides and sterically hindered amines is additionally added to the plastic recyclate.

25. A process according to claim 1, wherein at least one light stabilizer from the series consisting of the benzophenones, benzotriazoles, oxanilides and sterically hindered amines is additionally added to the plastic recyclate and the amount of the light stabilizer(s) is from 0.01 to 2 % by weight, based on the plastic recyclate.

26. A process according to claim 1, wherein a light stabilizer from the series consisting of the benzotriazoles and a light stabilizer from the series consisting of the sterically hindered amines are added.

27. A stabilizer mixture for recycled plastics, predominantly thermoplastics, obtained from

domestic, commercial or industrial waste or useful material collections, which comprises a) at least one sterically hindered phenol, b) at least one organic phosphorous or phosphonous ester and c) at least one metal salt of a fatty acid.

28. A stabilizer mixture according to claim 27, comprising per 100 parts

(A) as component a) 5-50 parts of pentaerythritol ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 5-50 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 5-50 parts calcium stearate;

(B) as component a) 5-50 parts of pentaerythritol ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 5-50 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 5-50 parts of a mixture of calcium and zinc stearates;

(C) as component a) 5-50 parts of octadecyl ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 5-50 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 5-50 parts of calcium stearate; or

(D) as component a) 10-40 parts of pentaerythritol ester of β -(3,5-di-tert.butyl-4-hydroxy-phenyl)-propionic acid, as component b) 10-40 parts of tris-(2,4-di-tert.butylphenyl)-phosphite and as component c) 20-50 parts of calcium stearate.

29. The use of a stabilizer mixture which comprises a) at least one sterically hindered phenol, b) at least one organic phosphorous or phosphonous ester and c) at least one metal salt of a fatty acid, for the stabilization of recycled plastics, predominantly thermoplastics, obtained from domestic, commercial and industrial waste.

30. A recycled plastic, predominantly a thermoplastic, obtained from domestic, commercial or industrial waste or useful material collections, which contains a) at least one sterically hindered phenol, b) at least one organic phosphorous or phosphonous ester and c) at least one metal salt of a fatty acid.

INTERNATIONAL SEARCH REPORT

Interr. al Application No
PCT/EP 93/02486

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08K5/00 C08L23/02 C08K5/09 C08K5/13 C08K5/524
C08K5/5393 //(C08K5/00,5:09,5:13,5:51)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,33 22 938 (BASF AG) 10 January 1985 see claims; example ---	1,27
X	DE,A,23 08 225 (AKZO GMBH) 6 September 1973 see claims; example 3 ---	1,27
X	CHEMICAL PATENTS INDEX, DOCUMENTATION ABSTRACTS JOURNAL Week 8909, Derwent Publications Ltd., London, GB; AN 89-066593 & JP,A,01 020 249 (NIPPON PETROCHEM K.K.) 24 January 1989 see abstract --- -/--	1,27

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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- *&* document member of the same patent family

Date of the actual completion of the international search

14 December 1993

Date of mailing of the international search report

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DE LOS ARCOS, E

INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/JP 93/02486

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	INDUSTRIE ANZEIGER vol. 99, no. 71 , 1977 pages 1367 - 1369 M. RIEDEL 'Neue Stabilisatoren zur Verbesserung des Recycling' see complete document, specially figure 2, examples 3, 4, 6 and 7 ---	1-30
X	CONF. INT. TRADE FAIR RECYCLING, REFUSE COLLECT. WASTE TREAT. "ELMIA AVFALL 79" 1979 , JÖNKÖPING, SWEDEN pages 657 - 667 F. MITTERHOFER 'Stabilization aspects for the recycling of plastic scrap and waste' see diagram 3; page 662, 1st. paragraph -----	1-30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 93/02486

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DE-A-2308225	06-09-73	GB-A- 1398281	18-06-75
		FR-A, B 2174850	19-10-73
		US-A- 3867325	18-02-75